

Synthesis of fluorinated hybrid material for UV embossing of a large core optical waveguide structure

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A new organic–inorganic hybrid material (HYBRIMER) has been synthesized homogeneously through a non-hydrolytic sol–gel process. The new HYBRIMER shows efficient index control and minor volume contraction behavior during micro-scale molding. In hybrid materials, the methacrylic end-group is considered suitable for cross-linking during the UV curing step, while the fluorinated functionality is appropriate for refractive index control. As the fluorinated silane contents are varied, the structural evolution and refractive index of the synthesized resin are then controlled (1.469 to 1.513 at 850 nm). A large core optical waveguide structure is formed by these hybrid materials, which exhibit low near IR wavelength absorption. A single material system is applied to both the core and the cladding materials of the optical waveguide. The measured optical propagation loss is lower than 0.25 dB cm^{-1} .

Introduction

A multimode optical waveguide consists of a large core structure on cladding, which is necessary for the access of network optical communication devices¹ or optical interconnection technology.² On the other hand, “HYBRIMERS” are organic–inorganic hybrid materials, which can be synthesized using a sol–gel process. In recent years, HYBRIMERS have gained increased popularity with regard to optical applications^{3–5} due to the advantages afforded by the combined properties of the organic flexibility of polymers and the inorganic thermal stability from the inorganic glass network⁶. The hydrolysis and condensation^{7,8} reactions, however, that are generated by the conventional sol–gel process result in synthesized HYBRIMERS that contain some residual solvent and water even after moderate evaporation.

In contrast to the conventional hydrolytic sol–gel process, the non-hydrolytic sol–gel process facilitates the synthesis of resin without leaving any trace of solvent. Thus, crack-free thick-coating films can be easily fabricated without abrupt shrinkage from non-hydrolytic sol–gel HYBRIMERS. Due to this crack-free pattern structure and minor volume contraction, HYBRIMERS synthesized by a non-hydrolytic sol–gel process are suitable for soft lithographic molding processes. Within the range of less than $1 \mu\text{m}$ to over $100 \mu\text{m}$, an embossed structure can be patterned without volume contraction depending on the master structure size. Large polymeric core optical waveguides have been fabricated by using soft lithographic methods.⁹ In addition, glass submicron fabrication has been carried out by micro-molding using the conventional sol–gel material.¹⁰ Nonetheless, there has been little effort thus far to apply these new methods to photo-curable non-hydrolytic sol–gel hybrid materials.¹¹

This study examines a fluorinated methacrylic HYBRIMER generated by the non-hydrolytic sol–gel process. This new HYBRIMER is characterized by the presence of fluorine functionality and a methacrylic polymerizable group. Diphenylsilanediol (DPSD) is composed of silanol groups, which can react with the alkoxy group of organo alkoxysilane, to form a siloxane bond. The alkoxysilane consists of perfluoro-alkylsilane (PFAS) and 3-(trimethoxysilyl)propyl methacrylate (MPTMS). Thus, fluorinated methacrylic polysiloxane resin can be synthesized through a poly-condensation reaction between the silanol groups of DPSD and the methoxy groups of MPTMS and PFAS. These reactions are briefly illustrated in Scheme 1.

This new HYBRIMER was synthesized in an effort to control the refractive index and to fabricate crack-free thick core structures by soft lithography. During the UV embossing process, the methacrylic polymerizable group of the fluorinated HYBRIMER is cross-linked by photo-polymerization. By changing the PFAS content, the reactivity and physical properties of the fluorinated HYBRIMER are then investigated. Using ^{29}Si NMR spectroscopy, formations of polysiloxane in the resins were confirmed. The physical properties of the fluorinated HYBRIMER, such as the refractive index of its thin film, near infrared light absorption, and the cutback loss of the fabricated optical ridge waveguide were investigated by controlling the PFAS content. It was discovered that the refractive index and near infrared light absorption decreased with an increase in the PFAS precursor content. The role of this PFAS precursor, which is composed of long perfluoro-alkyl chains of fluorinated HYBRIMER, was also examined by changing its concentration.

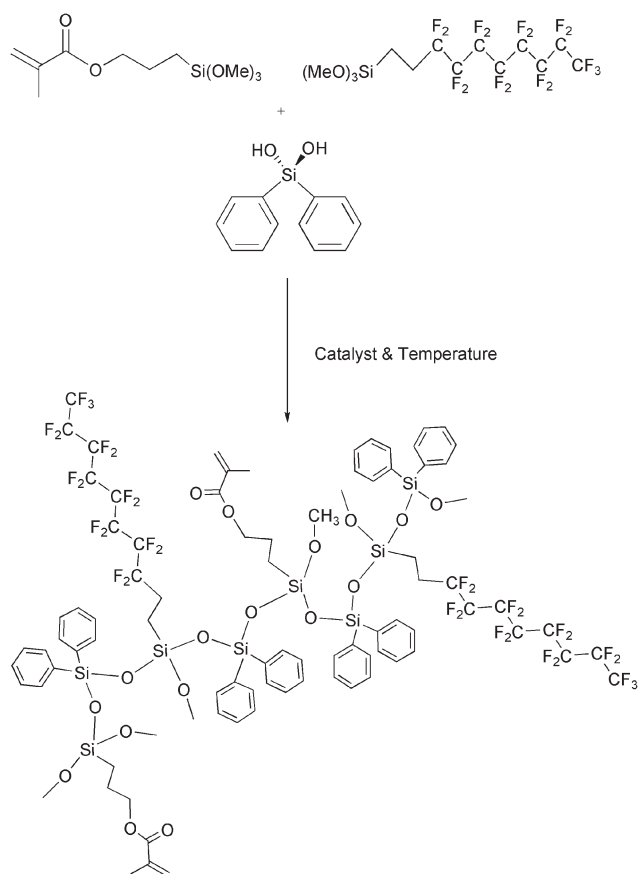
Experimental

Preparation of fluorinated HYBRIMER resin

In the experiment conducted for this study, 3-(trimethoxysilyl)propyl methacrylate (MPTMS, Aldrich),

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Scheme 1 Reaction scheme of silane precursors for the synthesis of fluorinated non-hydrolytic sol-gel hybrid materials.

(heptadecafluorodecyl)trimethoxysilane (PFAS, Toshiba), and diphenylsilanediol (DPSD, TCI) were used as precursor molecules without further purification, while barium hydroxide monohydrate ($\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$, Aldrich) was used as a catalyst to promote the poly-condensation reaction among these three precursors. The DPSD content was fixed at 50 mol% and the ratio of PFAS to MPTMS changed from 10 to 20 mol% of the entire precursors as shown in Table 1. Hence, the total proportion of MPTMS and PFAS together was 50 mol%. Barium hydroxide monohydrate (about 0.1 mol% of the precursors) was added as a catalyst. The catalyst was mixed only once in the first stage of resin preparation with PFAS precursor. First, PFAS and $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ were mixed, and DPSD and MPTMS were added continuously at 80 °C for two hours to prevent

Table 1 Characterization of fluorinated methacrylic HYBRIMERS

Notation	Ratio of PFAS Content (%)	Onset temperature of weight loss/°C ^a	Contact angle/° ^b
MFD _α	10	302	105
MFD _β	12.5	302	104.5
MFD _γ	15	310	105.5
MFD _δ	20	305	106

^a Determined by TGA at heating rate of 5 °C min⁻¹ in nitrogen.
^b Determined by contact angle measurement instrument KRÜSS GSA10.

self-condensation of DPSD and phase separation. The methanol, which is a by-product of the poly-condensation reaction among the three precursors, was extracted by vacuum heating. The reaction was kept steady at 80 °C for another two hours for complete poly-condensation. Finally, the solution was cooled to room temperature and filtered using a 0.45 μm size filter to remove the remaining $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ and dust. Thereafter, the obtained fluorinated methacrylic poly siloxane resin was mixed with a photoinitiator, Irgacure369 (Ciba Geigy), which facilitates curing by UV light during the UV embossing step. Table 1 shows the notation and characterization of the fluorinated resins based on the PFAS contents indicated in this study.

In order to investigate the properties of the resin, the fluorinated HYBRIMER was deposited onto p-type Si(100) wafers by spin coating at 2000 rpm for 30 seconds. These thin films were pre-dried at 80 °C for 3 minutes, and then cured by the UV light of a mercury lamp (365 nm wavelength). Finally, the films were cured thermally at 150 °C for 3 hours.

Characterization

²⁹Si NMR spectra of the resins from 30 vol% of the resin in chloroform-d were recorded using a Bruker FT 500MHz instrument. As a relaxation agent, chromium(III) acetylacetonate was added in concentrations of 30 mg l⁻¹. Pulse delays were set at 30 seconds. The sample temperature was controlled at 300 K, and TMS was used as a reference. The near IR spectra of the resins were obtained using a UV/VIS/NIR spectrophotometer (Shimadzu UV-3010PC) with a 1 cm path quartz cell. The scan interval was fixed at 2° throughout the measured range. The refractive indices of the HYBRIMER films were measured using a Metricon 2010 prism coupler, which generated light from a 0.85 μm laser diode, a 1.3 μm laser diode, and a 1.55 μm laser diode. The cleaved image of the ridge waveguide was examined using Scanning Electron Microscopy (Philips XL30SFEG). The optical propagation losses of the fabricated ridge waveguide were measured using cutback methods.¹² The incident light beam was introduced to the waveguides through a multi-mode fiber. The output beam power intensity was measured with an Anritsu optical power meter. The 55.5 mm long straight waveguide was cut by 10 mm, while the propagation loss was measured based on the difference between the input and the output light intensities using an optical power meter.

Results and discussion

Synthesis of fluorinated HYBRIMER resin

When the silanol group of DPSD reacts with the methoxy group of MPTMS and PFAS, a siloxane bond is formed among the precursors that produce methanol as a by-product. As this poly-condensation reaction takes place, the polysiloxane resin structure, which is composed of inorganic polysiloxane and methacrylic and perfluoroalkyl groups, is formed. Different reaction behaviors, however, may occur between the methoxy of MPTMS and PFAS and silanol of DPSD due to the steric hindrance caused by the perfluoroalkyl group from the PFAS precursor. Depending on the PFAS content, this

reactivity difference can be investigated using a ^{29}Si NMR tool. This poly-condensation reaction terminates after every silanol in DPSD disappears. In addition, the silanol groups in the oligomeric resin react with methanol and are transformed into methoxy groups *via* an esterification reaction.

^{29}Si NMR spectroscopy is considered an adequate method for the confirmation of poly-condensation reaction among the precursors. ^{29}Si NMR spectra of the resins with various compositions are shown in Fig. 1. The notation of the Si atom in NMR spectroscopy is represented as follows: D^n represents the silicon from DPSD while T^n represents the silicon from the combined MPTS and PFAS, where the superscript n denotes the number of siloxane bonds of the silicon. Table 2 shows the chemical shifts of silicon according to its bond states.

A small amount of D^0 species, diphenyldimethoxysilane (-29 ppm), which is produced from DPSD and methanol *via* an esterification reaction, remains in the resins of all the compositions. This indicates that the poly-condensation reaction of the precursor molecules has occurred effectively, and polysiloxanes have been formed in the resins. As the PFAS content increases, the particle size of the resin becomes smaller. This is due to a reduction in the degree of poly-condensation and the presence of more perfluoroalkyl groups, which sterically shield the methoxy groups. Thus, the silanol groups of DPSD cannot react completely with methoxy groups, while the T^3 species decreases in quantity with higher PFAS content. On the other hand, the methoxy group in the T^2 species is hydrolyzed by this water and is transformed into a silanol group. This silanol group in the T^2 species reacts with the methoxy group of the monomeric MPTS or PFAS. Hence, this mechanism converts the T^2 species into the T^3 species.¹³ The T^3 species, however, is present in much smaller quantities than those of the T^1 and T^2 species in the resin in all compositions. Since the poly-condensation reaction of the precursors was confirmed to have occurred effectively, the fluorinated methacrylic HYBRIMER resin was successfully synthesized. The fluorinated HYBRIMERS were composed of an inorganic polysiloxane chain inside, and methacryl, perfluoroalkyl, and phenyl groups outside, while the resin had low silanol content.

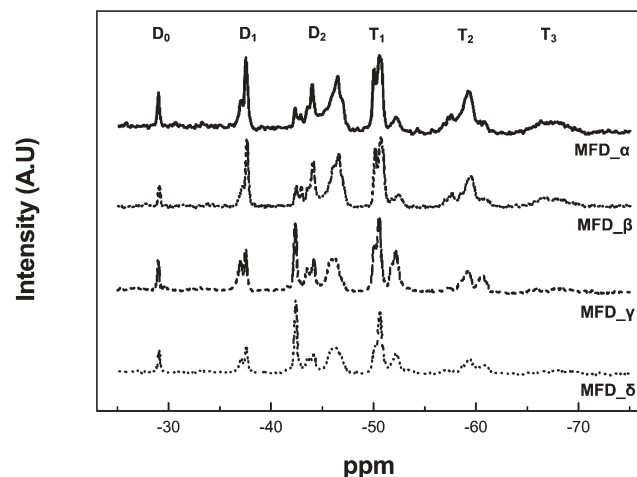


Fig. 1 ^{29}Si NMR spectra of the resins depending on composition.

Table 2 Chemical shifts of silicon according to its bond states

Species	Chemical shifts (ppm)
D^0 (diphenyldimethoxysilane)	-29
D^0 (diphenylsilanediol)	-34
D^1	-36 to -38
D^2	-42 to -47
T^1	-49 to -51
T^2	-57 to -61
T^3	-65 to -69

Characteristics of fluorinated HYBRIMER thick film

A thick film is formed evenly by single spin-coating, depending on the compositions. After thermal curing, no cracks appear while the volume contraction only measures -2.5% . Optical absorption is one of the dominant factors considered in the propagation loss of an optical waveguide. The fluorinated methacrylic HYBRIMER shows low optical absorption because it contains a small amount of Si-OH (at 3500 nm^{-1} in Fig. 2(b)). Moreover, in these fluorinated HYBRIMERS, C-H is partially substituted by C-F, which reduces the absorption over the whole detected spectral range. As shown in Fig. 2(a), there are strong absorption bands between 1100 nm and 1400 nm . The absorption of these wavelengths is determined by stretching vibrations and combination tones with deformation vibrations of carbon-hydrogen bonds

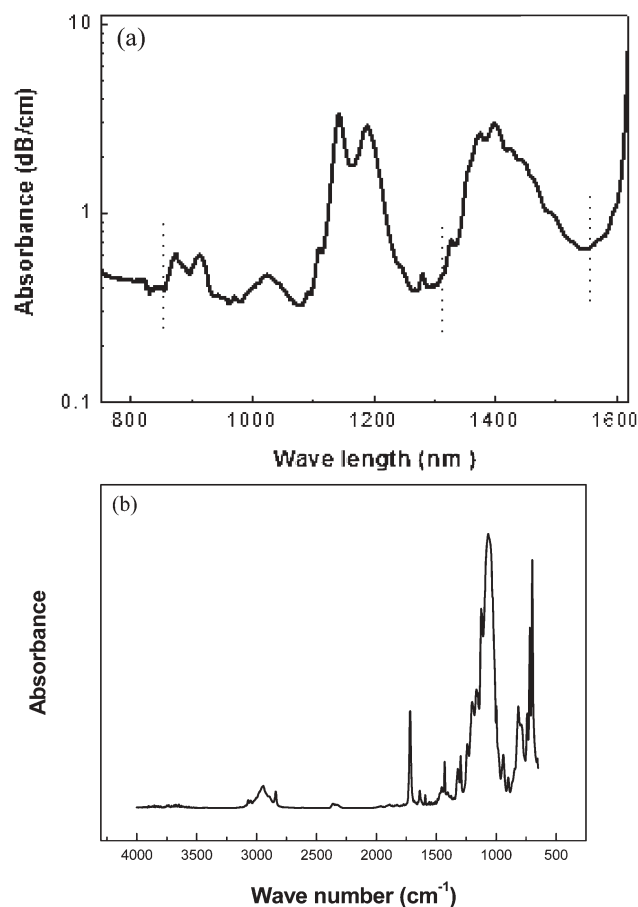


Fig. 2 (a) Near-IR absorption spectra of MFD $_{\alpha}$ resin, (b) FT-IR spectra of MFD $_{\alpha}$ resin.

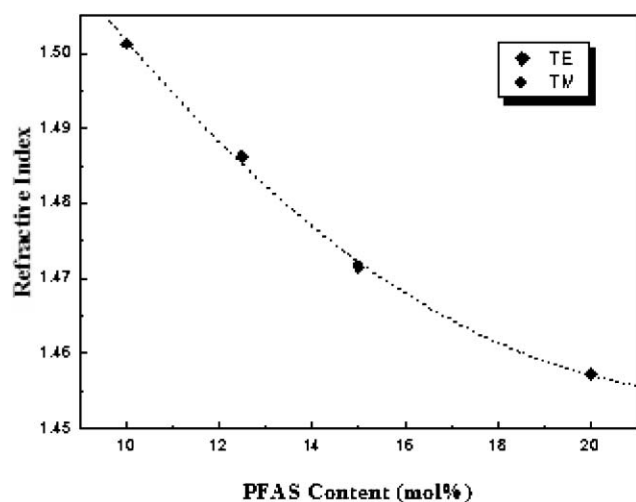


Fig. 3 Refractive indexes of fluorinated HYBRIMERS at 850 nm.

(C–H).¹⁴ In this study, the absorption of the fluorinated methacrylic HYBRIMER resulted in the following: 0.4 dB cm^{-1} at 850 nm, 0.4 dB cm^{-1} at 1310 nm, and 0.5 dB cm^{-1} at 1550 nm.

The perfluoroalkyl group has the ability to reduce the refractive index of the materials. Fig. 3 shows the changes in the refractive index of the HYBRIMER film as the PFAS content is increased at 850 nm. The refractive index measured using the prism coupler method is set as the average value for

the whole film thickness. The refractive index decreases from 1.5139 to 1.4693 based on variation of the PFAS content. As shown in Table 1, the onset temperature of weight loss of fluorinated HYBRIMERS is set at around $300\text{--}310 \text{ }^\circ\text{C}$, while the measured contact angle is around 105° in the various fluorinated HYBRIMERS, regardless of fluorine content. Due to their low contact angle throughout the composition, the fluorinated HYBRIMERS are suitable for hydrophobic coating applications.

Large core optical waveguide fabrication

The thickness and the refractive indices are designed such that they can determine the appropriate HYBRIMER in terms of satisfying the waveguide condition. In this study, the condition of the ridge waveguide is fixed, as shown in Fig. 4(a). The difference in the refractive index between core and cladding is 1%. The fluorinated methacrylic HYBRIMERS are used for the core and the cladding layers, depending on the HYBRIMER composition. MFD_α is used as the core material while MFD_β is employed as the cladding material.

First, the under-cladding layer is spin-coated on a silicon wafer and then cured by UV light. The core of the waveguide is formed by means of a soft-lithographic UV embossing method. The UV embossing process of the HYBRIMER is carried out with a flexible rubber mold. In the UV embossing method, the core HYBRIMER is spin-coated on the under-cladding layer. In addition, the PDMS mold is covered and pressed on the coated sample. The waveguides are formed by

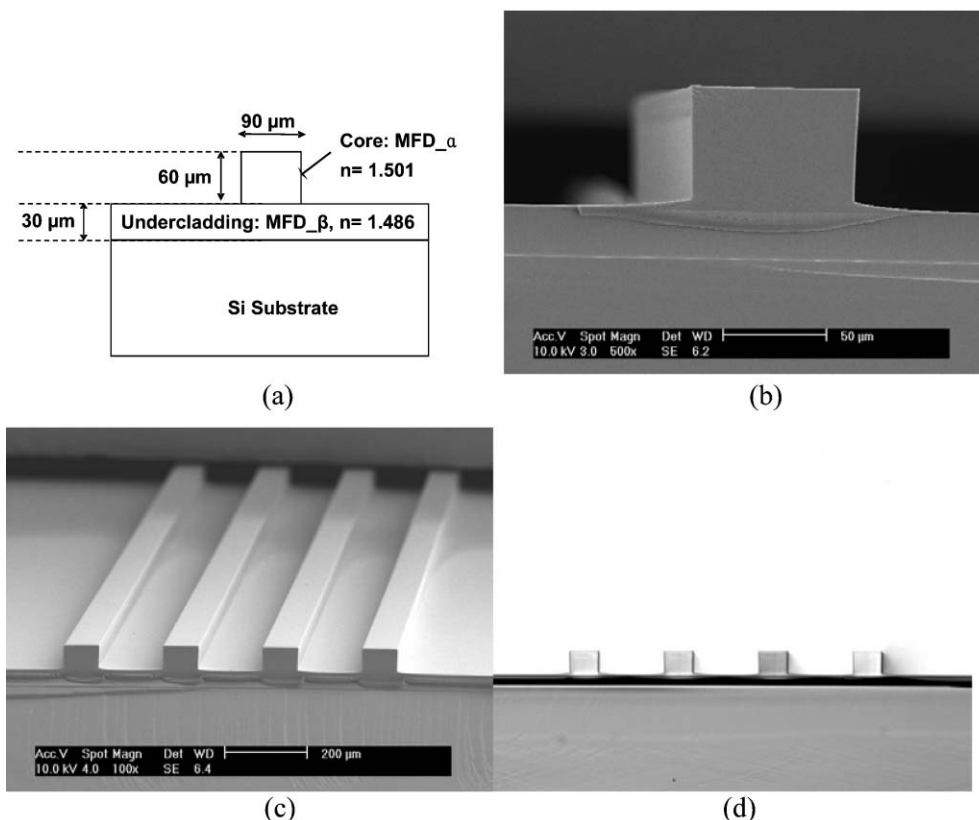


Fig. 4 (a) Design of the large core multi-mode optical waveguide, (b) SEM image of the cleaved edge of one waveguide, (c) SEM image of the fabricated ridge waveguide array, and (d) the light propagated image of the waveguide array.

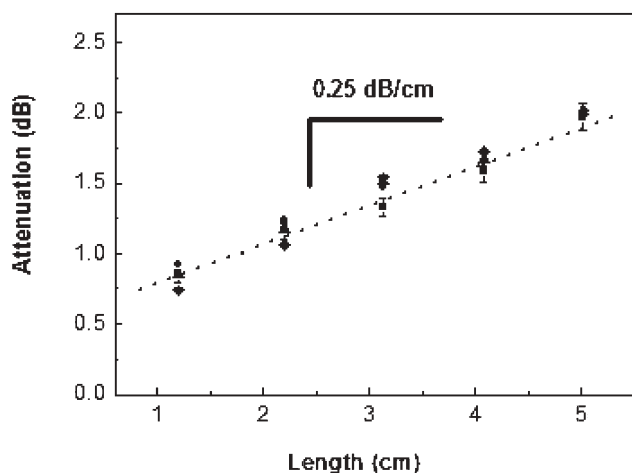


Fig. 5 Result of optical propagation loss of the fabricated waveguide.

applying pressure on the trenches of the mold. Meanwhile, the core material is polymerized by UV light to maintain the original replicated grooves. The appropriate amount of pressure should be applied as very high pressure will deform the patterns of the mold. After detaching the PDMS mold, the core of the replicated HYBRIMER waveguide is obtained. Finally, the fabricated ridge waveguide is thermally cured. The curing process of the waveguide structure is processed in two steps: soft baking at 80 °C and final curing at 150 °C to induce compatibility between the layers and to remove some solvents in the layers. There is a minimal residual layer between the core and the cladding layer, which does not raise any problems for our multimode waveguide (Fig. 4(b) and (c)). Furthermore, clear multimode propagation can be seen in Fig. 4(d). The average surface roughness of the fabricated waveguide, as measured by atomic force microscopy, is about 5 Å rms. As shown in Fig. 5, approximately 0.25 dB cm⁻¹ of propagation loss is measured in the 90 μm width waveguide at 850 nm wavelength. This value is lower than the absorption of the resin, since oligosiloxane in the resin polymerizes with polysiloxane during the curing of the film. Thus, the optical waveguides prepared from fluorinated HYBRIMERS can be considered potential candidates for various optical applications, such as optical interconnections at a wavelength of 850 nm.

Conclusions

The proposed new organic-inorganic hybrid material (HYBRIMER) synthesized in this study shows variable index control and little volume contraction. By varying the

fluorinated silane content, the reactivity of the synthesized resin and the refractive index could be controlled. The refractive index of this system could be varied from 1.469 to 1.513 within an 850 nm wavelength, depending on the fluorinated silane content. This single material system, in which the refractive indices are modified only by fluorinated silane content, was then applied to both the core and cladding materials of an optical waveguide. Approximately 0.25 dB cm⁻¹ of propagation losses was measured in the 90 μm width waveguide at 850 nm wavelength.

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